Markovnikov *versus* anti-Markovnikov hydrophosphination: Divergent reactivity using an iron(II) β-diketiminate pre-catalyst

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Abstract: The ability to tune between different regioselectivities using a common pre-catalyst is an unusual yet highly desirable process. Herein, we report the use of an iron(II) pre-catalyst that can be used to synthesize vinyl phosphines in a Markovnikov selective manner in benzene, whereas a simple change to dichloromethane as the reaction solvent leads to the *Z*-selective anti-Markovnikov functionalization. Preliminary mechanistic that studies suggest Markovnikov selectivity is a radical mediated process whereas the anti-Markovnikov selectivity is not radical in nature, and is due to a change in oxidation state, are reported.

The preparation of functionalized phosphorus-containing compounds is an important and necessary undertaking, leading to high value products for use in the chemical industries[1] including catalysis,[2] chemical biology,[3] polymer[4] and agrochemical sectors.[5] However, traditional methods for the preparation of functionalized phosphines can be limiting in terms of functional group tolerance and the quantity of waste generated.[6] For example, very often organometallic reagents such as Grignards are used to introduce functionality and many reactions release stoichiometric amounts of salt waste, which can lead to protracted purification processes, or they use P(V) reagents which need to be reduced to P(III). This limits both the usefulness and accessibility of such transformations. In contrast catalytic hydrophosphination displays excellent functional group tolerance and has the potential to be 100% atom economic.[7] In terms of alkyne hydrophosphination, examples of double hydrophosphination to form 1,2-diphos products and anti-Markovnikov mono-hydrophosphination catalysed by transition metals,[8] lanthanides[9] and main group[9d, 10] pre-catalysts exist. To the best of our knowledge, only two such examples have been reported using iron, both by Nakazawa and co-workers and both involve heating to 110 °C for several days (Scheme 1a).[11] However, a challenge that remains in the HP of alkynes is being able to selectively mono-hydrophosphinate in a Markovnikov fashion.[12] In terms of the HP of alkynes only one such example exists, which uses nickel catalysis, but with no analytical data, harsh reaction conditions and with moderate selectivity[8a] it seems fitting that a robust route to these challenging to prepare phosphines is sought. We herein report for the first time iron(II) catalyzed Markovnikov-selective hydrophosphination of alkynes under rapid and mild reaction conditions (Scheme 1b).

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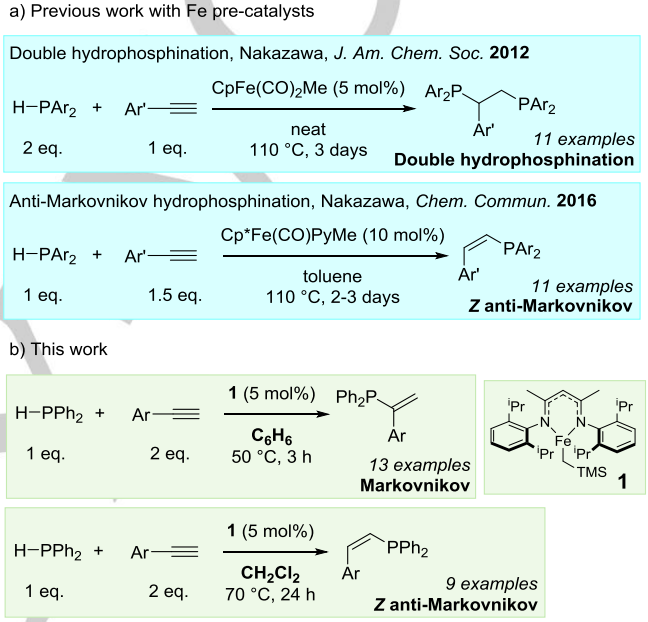
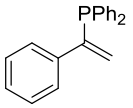
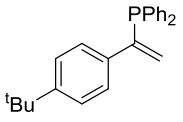
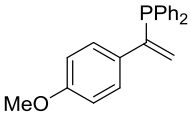
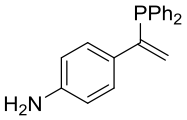
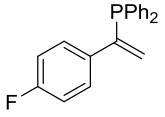
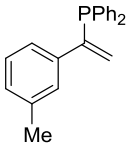
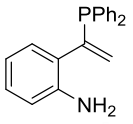
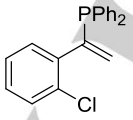
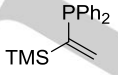
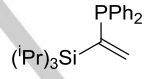
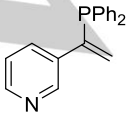
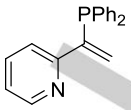
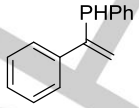
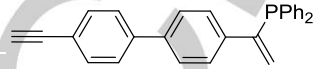
Remarkably, we also report an unprecedented solvent-mediated shift in regioselectivity from Markovnikov to *Z*-selective anti-Markovnikov hydrophosphination.



Scheme 1. a) Previous work in the field of iron catalyzed hydrophosphination of alkynes has allowed the development of double hydrophosphination and anti-Markovnikov *Z*-selective hydrophosphination. b) This work provides a comparatively mild route for Markovnikov and anti-Markovnikov hydrophosphination of alkynes.

Reacting $HPPh_2$ with phenyl acetylene in the presence of a catalytic amount of **1** in C_6H_6 leads to the formation of the Markovnikov product **2a** in a highly selective manner (Markovnikov:anti-Markovnikov 9:1, Table 1, Entry 1). After a short optimization process it was found that the reaction can be undertaken with 5 mol% **1**, 1 mmol alkyne, 0.5 mmol $HPPh_2$ in C_6H_6 in 3 h with a modest reaction temperature of 50 °C. It is worth noting that the reaction also works well at room temperature, whereby complete conversion to **2a** is obtained after 48 h with 5 mol% **1**. Use of a 2:1 ratio of phosphine:phenylacetylene does not promote the formation of the 1,2-diphosphosphane product (*cf.* Nakazawa),[11a] but instead leads to a mixture of tetraphenyldiphosphane ($Ph_2P–PPh_2$) and **2a**. Use of $FeCl_2$ does not lead to the formation of **2a**. With optimized conditions in hand we proceeded to explore the substrate scope for this transformation (Table 1).

Table 1. Markovnikov-selective hydrophosphination substrate scope.

Entry	Alkyne (RCCH) R =	Product		Yield (%)[a]
1	C_6H_5		**2a** **2a'**	100 (82) 100 (89)[b]
2	4-^{t}Bu-C_6H_4		**2b**	100 (75)
3[c]	4-MeO-C_6H_4		**2c**	100 (74)
4	4-H_2N-C_6H_4		**2d**	78
5	4-F-C_6H_4		**2e**	100 (80)
6	3-Me-C_6H_4		**2f**	88 (66)
7[d]	2-H_2N-C_6H_4		**2g**	33
8	2-Cl-C_6H_4		**2h**	no reaction
9[c],[e]	$(CH_3)_3Si$		**2i**	85 (60)
10[f]	(^{i}Pr$_3$)$_3$Si		**2j**	100
11[e]	C_6H_4N		**2k**	< 20
12	C_6H_4N		**2l**	< 20
13[g]	C_6H_5		**2m**	100 (81)
14	HCC(C_6H_4)$_2$		**2n**	100

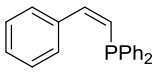
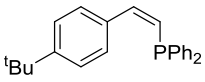
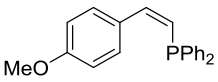
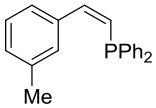
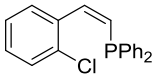
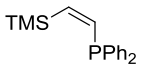
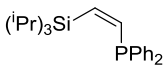
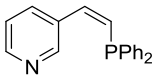
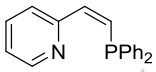
Reaction conditions: alkyne (1 mmol), $HPPh_2$ (87 µL, 0.5 mmol), **1** (14 mg, 5 mol%), C_6H_6 (350 µL), Ar, 50 °C, 3 h. 9:1 Markovnikov:anti-Markovnikov. [a] Spectroscopic yield calculated from the consumption of $HPPh_2$ against 1,3,5-trimethoxybenzene as an internal standard. All products isolated as the phosphine oxide unless stated otherwise (*see* supporting information), isolated yield shown in brackets. [b] Phenyl acetylene (1.1 mL, 10 mmol), $HPPh_2$ (870 µL, 5 mmol), **1** (140 mg, 5 mol%), C_6H_6 (3.5 mL), Ar, 50 °C, 24 h. Only trace anti-Markovnikov observed. Isolated as the P(III) product. [c] Isolated as the P(III) product. [d] Mixture of Markovnikov and anti-Markovnikov products. [e] 70 °C, 24 h. [f] 90 °C, 24 h. [g] Mixture of mono:di alkenyl product (85:15).

Aryl acetylenes with a range of electronic properties are tolerated in the reaction, giving a high spectroscopic and isolated yield of product. The reaction also responds well to scale-up. When the reaction is performed using 5 mmol $HPPh_2$ (0.93 g), complete conversion to the Markovnikov product is obtained in 24 h and can be isolated cleanly as the P(III) compound in high yield (1.29 g, 89%, **2a'**, Table 1, Entry 1). Strongly electron donating (**2c**, Entry 3) and electron withdrawing (**2e**, Entry 5) groups can be used and, unusually, 4-aminophenyl acetylene with its free functionality primed for further transformations, also generates a high yield of the desired Markovnikov product (**2d**, Entry 4). In contrast, substitution in the *ortho*-position is not suitable for this transformation (compare Entries 4 to 7 and 5 to 8). In the case of both 2-amino-phenylacetylenes and 2-chloro-phenylacetylenes, no unwanted side-reactions take place and therefore it can be assumed that steric bulk and/or competing heteroatom coordination inhibits reactivity. Silylacetylenes give high yield of the desired product (Entries 9 and 10), but unfortunately *meta*- and *ortho*-pyridyl substrates are not good reagents for this transformation. Again this is presumably due to deactivation of the alkyne (*meta*) or competing coordination (*ortho*). We are pleased to report that H_2PPh can be used to functionalize phenylacetylene with a high level of mono-hydrophosphination selectivity (85:15 mono:di, Entry 13) whilst use of a diyne can lead to selective single-hydrophosphination in the presence of diphenylphosphine (Entry 14).

We have previously reported a change in chemoselectivity with **1** when the solvent is changed.[13] Interested in the potential of exploiting this further, we undertook the same alkyne hydrophosphination transformation in CH_2Cl_2. Although more forcing conditions are necessary, a complete switch in regioselectivity is observed and the anti-Markovnikov product forms as, predominantly, the *Z*-isomer. Again, a wide variety of alkynes can be used in this transformation with the vast majority of products obtained in excellent yield (Table 2).[14] It is worth noting the higher yields obtained with the 2-chloro substrate

(product **3e**, Entry 5) and pyridylacetylenes (Entries 8 and 9). These results might indicate that the potential for competing coordination to iron and catalyst inhibition/deactivation is not a limiting factor in this reaction mechanism.[15]

Table 2. Markovnikov-selective hydrophosphination substrate scope.

Entry	Alkyne (RCCH) R =	Product		Yield (%)[a]
1	C_6H_5		**3a**	100 (86)
2	4-^{t}Bu-C_6H_4		**3b**	100 (68)
3	4-MeO-C_6H_4		**3c**	66
4	3-Me-C_6H_4		**3d**	72 (56)
5	2-Cl-C_6H_4		**3e**	56 (49)
6[b]	$(CH_3)_3Si$		**3f**	100 (55)
7[b]	^{i}Pr$_3$Si		**3g**	100 (88)
8	C_6H_4N		**3h**	100 (77)
9	C_6H_4N		**3i**	26

Reaction conditions: alkyne (1 mmol), $HPPh_2$ (87 µL, 0.5 mmol), **1** (14 mg, 5 mol%), CH_2Cl_2 (350 µL), Ar, 70 °C, 24 h. 95:5 *Z*:*E*, except Entries 1, 6, 7 (9:1 *Z*:*E*). [a] Spectroscopic yield calculated from the consumption of $HPPh_2$ against 1,3,5-trimethoxybenzene as an internal standard. All products isolated as the phosphine oxide unless stated otherwise (*see* supporting information), isolated yield shown in brackets. [b] 90 °C, 24 h.

Intrigued by the contrasting selectivities and the different mechanisms that must be at play, we sought to explore the mechanism through stoichiometric reactions and simple reaction monitoring studies. The Markovnikov catalysis undergoes a striking color change, where the pre-catalyst is yellow in color, but the reaction mixture on the addition of the reagents turns red, then darkens to brown over the course of the reaction. A stoichiometric reaction of **1** with phenylacetylene in C_6H_6 results in a solution which can be crystallized by slow evaporation to give dark orange plate-like crystals. Single crystal X-ray diffraction reveals an iron acetylide dimer (**4**, Figure 1).[16] The end-on bound acetylene units have carbon-carbon triple bond lengths of 1.223(3) Å (C30-C31), similar to those observed for a standard *sp* hybridized carbon-carbon bond, although the C30-C31-C32 bond angle has distorted from linearity to 159.7(2) °.

By using a pure sample of **4** in catalysis under standard Markovnikov hydrophosphination conditions and comparing it to catalysis performed by **1**, only 33% **2a** is obtained (Figure 2, ◆ (catalyzed by **1**) and ◆ (catalyzed by **4**)). This would suggest that **4** is not an on-cycle intermediate. Leaving the reaction mediated by **4** for an extended period of time (to allow for the splitting of the dimer which may be slow) does not lead to a considerably greater amount of **2a** to be formed.

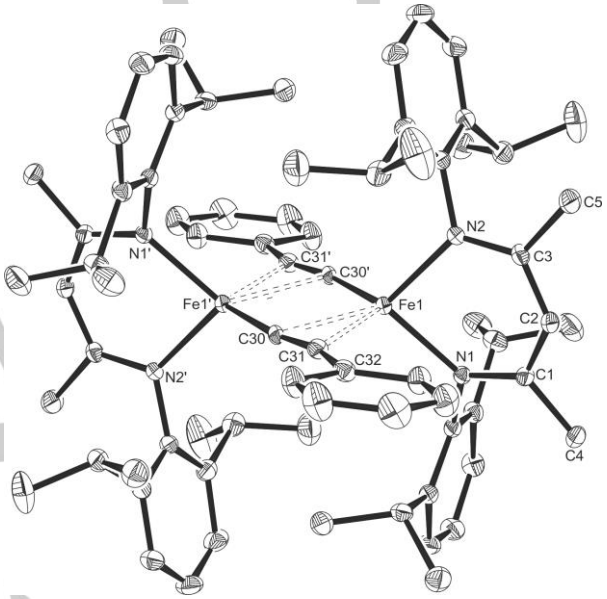


Figure 1. Molecular structure of complex **4**. Ellipsoids are represented at 50%. Hydrogen atoms omitted for clarity.

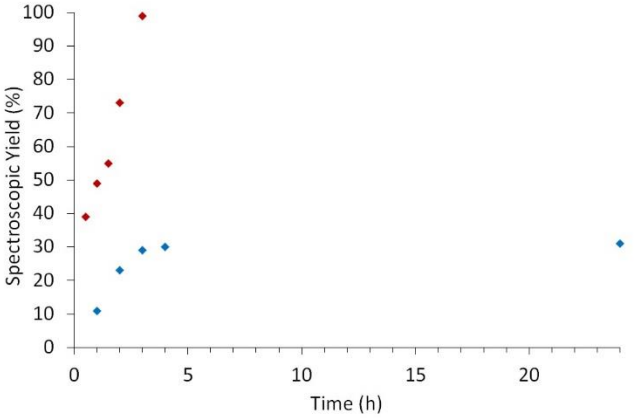
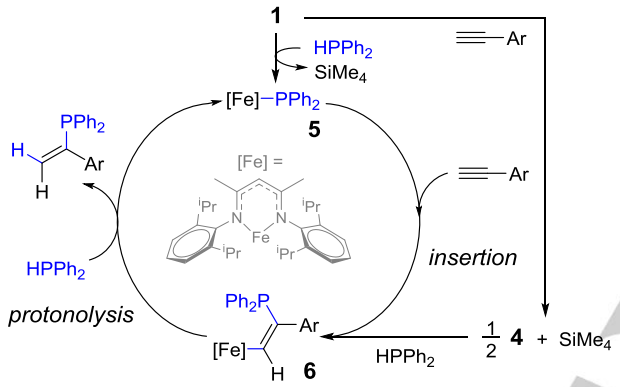


Figure 2. Reaction monitoring for the formation of **2a** using 5 mol% **1** (◆) and 2.5 mol% **4** (◆).

We tentatively postulate a catalytic cycle which could involve **4** as an off-cycle species which only forms in minor quantities (Scheme 2). The productive catalytic pathway involves the formation of an iron phosphido intermediate (**5**), which then reacts with alkyne to form an iron alkenyl[17] intermediate (**6**), where regioselectivity is driven by sterics. Protonolysis releases the product and regenerates **5**. The iron phosphido has not been isolated from

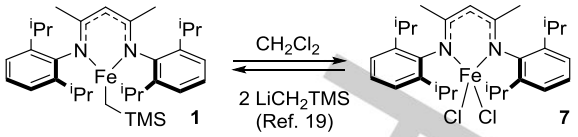
stoichiometric reactions because competitive and rapid dehydrocoupling takes place within minutes at room temperature to form $Ph_2P–PPh_2$.[13] However, it is evident that under catalytic conditions C–P bond formation is more favorable than P–P bond formation. When the concentration of alkyne is increased the rate of reaction is suppressed, suggesting that the off-cycle formation of **4** starts to dominate. No catalysis takes place with $Ph_2P–PPh_2$ as the phosphorus source, but the reaction is quenched by the addition of a radical clock suggesting radicals play a role, but their function is as yet undetermined. In this regard, it is important to note that use of AIBN (20 mol%) in the absence of **1** under Markovnikov reaction conditions gives 98% anti-Markovnikov product (**3a**) with several other species formed in trace amounts, including **2a**,[18] suggesting that **1** is inherently involved in bond formation and does not merely act to generate phosphinyl radicals in solution.



Scheme 2. Tentative mechanism for Markovnikov selective hydrophosphination of alkynes.

The change in selectivity observed in CH_2Cl_2, we believe, can be attributed to a change in oxidation state of the metal complex. Hessen has previously shown that Fe(III) complex **7** can be alkylated with concomitant reduction using $LiCH_2TMS$.[19] It is therefore not surprising that the reverse reaction, whereby halide abstraction from the reaction solvent with oxidation of **1**,[20] leads to the formation of **7** (Scheme 3). Reaction of **1** in CH_2Cl_2 at 50 °C leads to a color change from yellow to green, synonymous with the formation of **7**. The new complex is also NMR silent, indicative of a highly paramagnetic Fe(III) species. We do not believe that radicals are involved in catalytic anti-Markovnikov hydrophosphination because once the reaction has been initiated, where **7** has formed *in situ* and **3a** has started to be generated during catalysis, addition of (chloromethyl)cyclopropane as a radical clock has no effect on the reaction.

Use of an independently synthesized[21] sample of **7** in a reaction monitoring study shows that catalysis performed by **7** closely matches the catalytic competency of **1** in CH_2Cl_2 (Figure 3). We believe that this is a case of Lewis acid-type activation of the alkyne followed by nucleophilic attack by the phosphine. $FeCl_3$ as the pre-catalyst leads to 56% **3a** and although lower than that obtained with **1**, solubility is likely to be limiting in this case.



Scheme 3. Formation of **7** is possible using dichloromethane as the halide source and the oxidant.

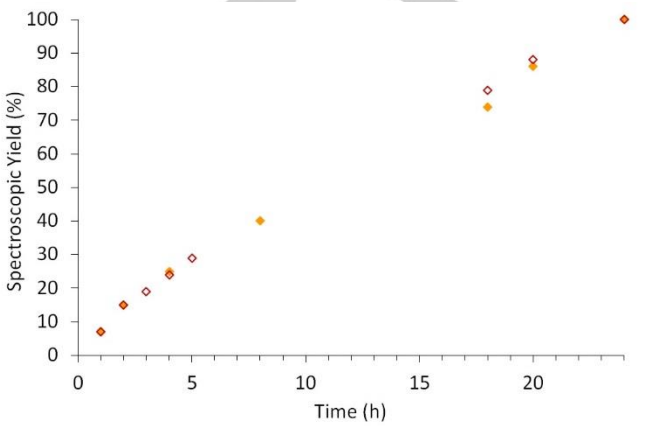


Figure 3. Reaction monitoring for the formation of **3a** using 5 mol% **1** (◇) and 5 mol% **7** (◆).

In conclusion we have shown that from one common pre-catalyst we can undertake divergent reactivity which is dictated by the choice of solvent. The highly unusual Markovnikov hydrophosphination product is formed in benzene and the anti-Markovnikov product forms in dichloromethane. Preliminary mechanistic studies would suggest that the source of these different modes of reactivity are linked to oxidation state and the mode of the C–P bond forming process. Fe(II) and radicals are implicated in Markovnikov selective reactions, whereas for anti-Markovnikov selectivity Fe(III) is generated and radicals are not involved in C–P bond formation. The fact that such a vast change in regioselectivity is observed with just a simple change in solvent raises the question of what other iron catalyzed transformations can be attenuated in this way.

Experimental Section

General reaction procedure Pre-catalyst **1** (14 mg (0.025 mmol, 5 mol%) was added to a Schlenk tube under an atmosphere of argon along with 0.35 mL of C_6H_6 or CH_2Cl_2. Alkyne (1 mmol) and $HPPh_2$ (87 µL, 0.5 mmol) were then added to the reaction vessel and the corresponding solution was stirred at 50 °C for 3 h (C_6H_6) or at 70 °C for 24 h (CH_2Cl_2) (unless stated otherwise). Crude reaction mixtures were exposed to air and worked up on the bench. In reactions where phosphine substrates are not fully consumed the crude mixture was first eluted on silica gel (petroleum ether) to remove the unreacted phosphine, a second fraction was then taken using diethyl ether (Et_2O) as the eluent. Hydrogen peroxide (30% in H_2O) was added to the Et_2O phase and the solution stirred for 5-10 minutes. Stirring was then ceased and the solution quenched with de-ionised water. The layers were then separated and the aqueous layer was washed with diethyl ether (2 x 20mL) and the organic layers combined, dried over

$MgSO_4$ and filtered. Volatiles were then removed *in vacuo* and products were isolated by flash chromatography on silica gel (Et_2O).

Acknowledgements

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Keywords: homogeneous catalysis • iron • phosphanes • phosphaalkenes • hydrophosphination

[1] J. A. Kent, *Kent and Riegel's Handbook of Industrial Chemistry and Biotechnology*, Springer, Dordrecht, **2010**.

[2] P. C. J. Kamer and P. W. N. M. v. Leeuwen, *Phosphorus(III) Ligands in Homogeneous Catalysis: Design and Synthesis*, Wiley-VCH, Weinheim, **2012**.

[3] W. J. Stec, *Phosphorus Chemistry Directed Towards Biology*, Pergamon Press, New York, **1979**.

[4] S. Monge and G. David, *Phosphorus-Based Polymers: From Synthesis to Applications*, Royal Society of Chemistry, Cambridge, **2014**.

[5] a) F. Müller, *Agrochemicals: composition, production, toxicology, applications*, Wiley-VCH, Weinheim, **2000**; b) E. Bünemann, *Phosphorus in Action Biological Processes in Soil Phosphorus Cycling*, Springer, Berlin, Heidelberg, **2011**.

[6] I. Wauters, W. Debrouwer and C. V. Stevens, *Beilstein J. Org. Chem.* **2014**, *10*, 1064-1096.

[7] a) O. Delacroix and A. C. Gaumont, *Curr. Org. Chem.* **2005**, *9*, 1851-1882; b) S. Greenberg and D. W. Stephan, *Chem. Soc. Rev.* **2008**, *37*, 1482-1489; c) L. Rosenberg, *ACS Catal.* **2013**, 2845-2855; d) V. Koshti, S. Gaikwad and S. H. Chikkali, *Coord. Chem. Rev.* **2014**, *265*, 52-73; e) C. A. Bange and R. Waterman, *Chem. Eur. J.* **2016**, *22*, 12598-12605.

[8] a) M. A. Kazankova, I. V. Efimova, A. N. Kochetkov, V. V. Afanas'ev, I. P. Beletskaya and P. H. Dixneuf, *Synlett* **2001**, 497-500; b) M. A. Kazankova, I. V. Efimova, A. N. Kochetkov, V. V. Afanas'ev and I. P. Beletskaya, *Russ. J. Org. Chem.* **2002**, *38*, 1465-1474; c) F. Jerome, F. Monnier, H. Lawicka, S. Derien and P. H. Dixneuf, *Chem. Commun.* **2003**, 696-697; d) H. Ohmiya, H. Yorimitsu and K. Oshima, *Angew. Chem. Int. Ed.* **2005**, *44*, 2368-2370; e) A. A. Kissel, T. V. Mahrova, D. M. Lyubov, A. V. Cherkasov, G. K. Fukin, A. A. Trifonov, I. Del Rosal and L. Maron, *Dalton Trans.* **2015**, *44*, 12137-12148; f) C. A. Bange and R. Waterman, *ACS Catal.* **2016**, *6*, 6413-6416; g) A. Di Giuseppe, R. De Luca, R. Castarlenas, J. J. J. Perez-Torrente, M. Crucianelli and L. A. Oro, *Chem. Commun.* **2016**, *52*, 5554-5557; h) h) J. Yuan, L. Zhu, J. Zhang, J. Li and C. Cui, *Organometallics* **2017**, *36*, 455-459.

[9] a) K. Takaki, M. Takeda, G. Koshoji, T. Shishido and K. Takehira, *Tetrahedron Lett.* **2001**, *42*, 6357-6360; b) K. Takaki, K. Komeyama and K. Takehira, *Tetrahedron* **2003**, *59*, 10381-10395; c) K. Takaki, G. Koshoji, K. Komeyama, M. Takeda, T. Shishido, A. Kitani and K. Takehira, *J. Org. Chem.* **2003**, *68*, 6554-6565; d) H. Hu and C. Cui, *Organometallics* **2012**, *31*, 1208-1211; e) J. Yuan, H. Hu and C. Cui, *Chem. Eur. J.* **2016**, *22*, 5778-5785.

[10] J. P. W. Stelmach, C. A. Bange and R. Waterman, *Dalton Trans.* **2016**, *45*, 6204-6209.

[11] a) M. Kamitani, M. Itazaki, C. Tamiya and H. Nakazawa, *J. Am. Chem. Soc.* **2012**, *134*, 11932-11935; b) M. Itazaki, S. Katsube, M. Kamitani and H. Nakazawa, *Chem. Commun.* **2016**, *52*, 3163-3166.

[12] Markovnikov and anti-Markovnikov hydrophosphination of alkenes has been achieved with iron pre-catalysts. $FeCl_2$ gives Markovnikov product and $FeCl_3$ gives anti-Markovnikov product: L. Routaboul, F. Toulgoat, J. Gatignol, J.-F. Lohier, B. Norah, O. Delacroix, C. Alayrac, M. Taillefer and A.-C. Gaumont, *Chem. Eur. J.* **2013**, *19*, 8760-8764.

[13] A. K. King, A. Buchard, M. F. Mahon and R. L. Webster, *Chem. Eur. J.* **2015**, *21*, 15960-15963.

[14] Catalyst-free alkyne HP has been reported by Alonso and co-workers at 70 °C (neat reaction conditions, overnight reaction). See: a) F. Alonso, Y. Moglie, G. Radivoy and M. Yus, *Green Chem.* **2012**, *14*, 2699-2702; b) Y. Moglie, M. J. Gonzalez-Soria, I. Martin-Garcia, G. Radivoy and F. Alonso, *Green Chem.* **2016**, *18*, 4896-4907. Catalyst-free reactions in CH_2Cl_2 give poor yields (Ref. 13).

[15] Aliphatic alkynes such as ethynylcyclopentane and 1-hexyne do not undergo hydrophosphination under any of the standard reaction conditions. No reaction is observed between $HPCy_2$ and phenylacetylene under the optimized Markovnikov or anti-Markovnikov conditions.

[16] Crystal data for **4** ($C_{74}H_{92}Fe_2N_4$, CCDC 1521799). M = 1149.21, λ = 1.54184, monoclinic, space group P 1 21/n 1, *a* = 13.9894(4), *b* = 13.2581(4), *c* = 17.8087(5) Å, α = 90, β = 97.573(3), γ = 90 °, U = 3274.22(16) $Å^3$, *Z* = 2, ρ_{cald} = 1.166 gcm^{-3}, μ = 3.873 mm^{-1}, F(000) = 1232. Crystal size = 0.209 x 0.128 x 0.031 mm, unique reflections = 21950, observed reflections [$I>2\sigma(I)$] = 5249, data/restraints/parameters = 6454/0/371. Observed data; R1 = 0.0427, wR2 = 0.0941. All data; R1 = 0.0571, wR2 = 0.1003. Max peak/hole = 0.290 and −0.259 $eÅ^{-3}$, respectively.

[17] a) O. S. Mills and A. D. Redhouse, *Chem. Commun.* **1966**, 444-445; b) O. S. Mills and A. D. Redhouse, *J. Chem. Soc. A.* **1968**, 1282-1292; c) D. F. Marten, E. V. Dehmlow, D. J. Hanlon, M. B. Hossain and D. Van der Helm, *J. Am. Chem. Soc.* **1981**, *103*, 4940-4941; d) M. P. Gamasa, J. Gimeno, E. Lastra, M. Lanfranchi and A. Tiripicchio, *J. Organomet. Chem.* **1992**, *430*, C39-C43.

[18] See supporting information.

[19] T. J. J. Sciarone, A. Meetsma and B. Hessen, *Inorg. Chim. Acta* **2006**, *359*, 1815-1825.

[20] a) S. O. Obare, T. Ito and G. J. Meyer, *J. Am. Chem. Soc.* **2006**, *128*, 712-713; b) H. Song and E. R. Carraway, *Environ. Eng. Sci.* **2006**, *23*, 272-284; c) S. J. Bransfield, D. M. Cwiertny, K. Livi and D. H. Fairbrother, *Appl. Catal., B.* **2007**, *76*, 348-356; d) S. El-Tarhuni, M. Ho, M. H. Kawser, S. Shi and M. W. Whiteley, *J. Organomet. Chem.* **2014**, *752*, 30-36.

[21] A. Panda, M. Stender, R. J. Wright, M. M. Olmstead, P. Klavins and P. P. Power, *Inorg. Chem.* **2002**, *41*, 3909-3916.

Entry for the Table of Contents

COMMUNICATION

Highly selective Markovnikov alkyne hydrophosphination is reported in benzene, whereas on changing the reaction solvent to dichloromethane the selectivity switches to give the *Z* anti-Markovnikov product. Preliminary mechanistic insight reveals that a change in metal oxidation state may be responsible for the divergent reactivity observed.

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Markovnikov *versus* anti-Markovnikov hydrophosphination: Divergent reactivity using an iron(II) β-diketiminate pre-catalyst